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Palladium nanoparticles embedded on thiourea-modified chitosan: a green and sustainable heterogeneous catalyst for the Suzuki reaction in water†

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Palladium nanoparticles (PdNPs) embedded on thiourea modified chitosan (TMC) are prepared in spherical and cubical shapes by intercalating palladium(II) acetate in TMC, a natural bio-polymer, and a subsequent reduction using ellagic acid (EA) as a natural and green reducing source in water. The formation of palladium nanoparticles in water is monitored by UV-Vis, spectroscopy and the PdNPs/TMC solid matrix are characterized by FT-IR, powder XRD and HR-TEM. The amount of palladium entrapped on TMC is measured by ICP-OES analysis, and it is found to be 0.00103 mol%. The synthesised PdNPs/TMC reported for the first time, were employed as heterogeneous catalysts for Suzuki cross-coupling reactions of aryl iodide/bromide with various substituted aryl boronic acids in water and showed high catalytic activity under mild reaction conditions. Easy separation, the absence of an inert atmosphere and good to excellent yields are the other significant outcomes of this protocol. In addition, the reactions also work well with various heterocyclic boronic acids. Also the catalyst can be easily recovered and reused for at least five runs without loss in its activity.

Introduction

The development of greener methods for the efficient synthesis of well characterized metal nanoparticles has become a major focus in nanoscience.[1] Researchers have explored the potential of nanomaterials for various applications such as optoelectronics,[2] drug delivery,[3] sensors,[4] catalysis,[5] tissue engineering,[6] biological labels[7] and magnetic resonance imaging (MRI) contrast enhancement. Controlling the shape and size of crystalline nanomaterials has attracted particular interest, due to their tunable nature during their fabrication.[8] Mild, biomimetic and eco-friendly approaches have been gaining importance[9] due to their ability to form dimension controlled arrays of a wide range of nanomaterials, thus providing simple and cost-effective methods, which could potentially be employed in large-scale production.[10] Greener methods have been followed for synthesis of silica structures such as nanospheres, nanoplates, nanocylinders and nanotubes.[11–15] Currently, several 'green' reducing agents such as polyphenols, enzymes, citric acid, vitamins (B, C, D and K) are employed for synthesis of shape selective silver, palladium and gold nanoparticles.[16]

Biodegradable polymers are able to stabilize and functionalize metal nanoparticles without any undesirable consequences on the environment and biosystems.[17] Various stabilizing agents are available to prevent the nanoparticles from aggregation as well as to functionalize the particles for the desired applications.[18] Pd(II)/chitosan catalyst has already been tested as a heterogeneous catalyst in microwave-assisted reactions.[19] Although chitosan modification requires some tricky procedures,[20] this material is cheap, stable and biodegradable, making it suitable for greener Pd-catalyzed Suzuki reactions.[21–25] Poor solubilizing of chitosan in many organic solvents make it as an excellent supports for various organic transformations.[26–28] The ultrasound assisted cross-linking of chitosan with hexamethylene diisocyanate with the simultaneous incorporation of $Pd(OAc)_2$ is reported in the solid-state Suzuki cross-coupling.[29]

Palladium catalyzed carbon–carbon coupling Suzuki–Miyaura reactions of aryl halides are very important and a versatile route to construct biaryl units.[30,31] Although homogeneous palladium catalysts have been extensively investigated, these reactions remain challenging due to cost of catalyst, lack of reusability and difficulty to separate from the reaction mixture[32] which are the notable drawbacks in the pharmaceutical industry. To overcome those problems, heterogeneous

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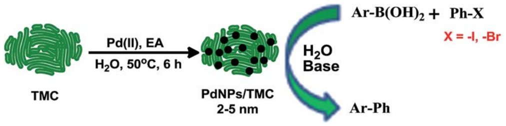


Scheme 1 Green synthesis and stabilization of PdNPs used as heterogeneous catalyst for Suzuki reaction.

palladium catalysts provide a promising solution and a number of solid materials such as carbon structures[33,34] polymers[35,36] have been employed as supports for palladium nanoparticles.[37–44] Among the several supports examined, chitosan displayed better performances providing a prompt anchorage to Pd nanoparticles.

Though chitosan have more number of amino (–NH$_2$) and hydroxyl (–OH) functional groups, increasing attention has been paid to thiourea modification, which can provide more metal binding sites.[45] Due to its strong affinity for palladium,[46] chitosan and modified chitosan has been used as supramolecular ligand for the coupling reaction. Lee *et al.* used chitosan supported Pd nanoparticles for Suzuki coupling in water. But this reaction needed heating at 150 °C under microwave irradiation for 15 h.[47] Also the same group used PEG-chitosan for the same reaction. This method also has a disadvantage that the recyclability of catalyst was very poor. A significant decrease in yield was observed after only two reaction cycles.[48] Recently Monopoli *et al.*, carried out Suzuki coupling in ionic liquid as solvents using chitosan supported PdNPs. In this method, it needs 110 °C for the activation.[49] In addition, all the above methods need either conventional reducing agent such as hydrazine or additive TBAB. There is a high demand for simple, inexpensive and easily accessible catalysts for these coupling reactions. Here, we report the green synthesis and stabilization of PdNPs on thiourea modified chitosan (TMC) under mild conditions *via* naturally occurring ellagic acid as green reducing agent.

Initially palladium(II) acetate is intercalated onto TMC biopolymer to form the Pd(II)/TMC complex which is subsequently reduced by EA to form the heterogeneous catalyst PdNPs/TMC (Scheme 1). This is used as a catalyst for the Suzuki carbon–carbon coupling reaction between aryl iodide and bromide with various substituted boronic acids under mild reaction conditions in water.

Results and discussion

As chitosan derivatives have high sorption capacity towards metals during immobilization and are water compatible, one of the chitosan derivative called TMC (thiourea modified chitosan) was prepared,[50] and it is used as support for PdNPs. EA (ellagic acid) is found to have good capability for reducing palladium ions, resulting in the formation of PdNPs. They are also found to recognize and affect the further growth of PdNPs on the 200, 220 and 111 faces, leading to the formation of spherical and cube shaped PdNPs.

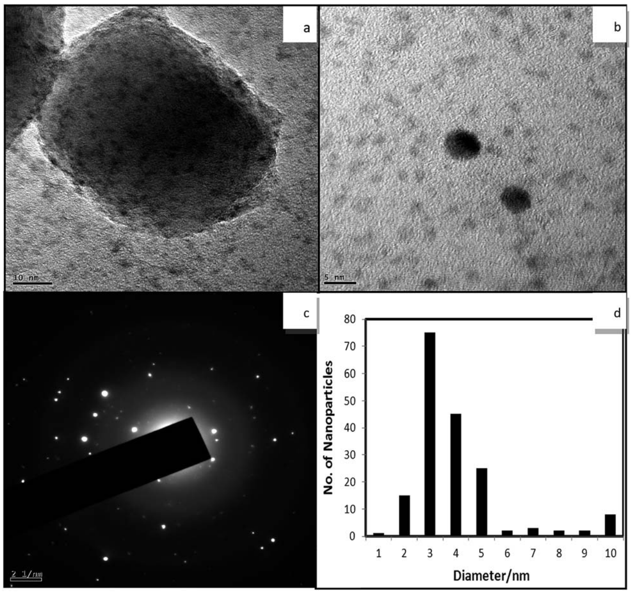


Fig. 1 (a) TEM image of heterogeneous catalyst PdNPs/TMC (b) HR-TEM image of PdNPs/TMC (spherical nanoparticles around 3–5 nm) (c) SAED image of PdNPs/TMC catalyst (d) histogram of PdNPs/TMC heterogeneous catalyst.

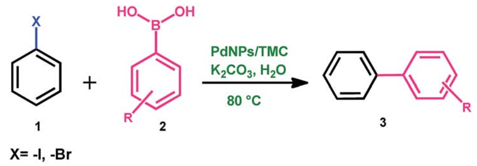
Table 1 Optimization of reaction conditions for Suzuki reaction[a]

S. no.	Catalyst	Base	Solvent	Yield[b]
1	—	K_2CO_3	Water	Nil[c]
2	$Pd(OAc)_2$[d]	K_2CO_3	Water	26
3	TMC/$Pd(OAc)_2$[e]	K_2CO_3	Water	43
4	EA/Pd(II)[f]	K_2CO_3	Water	49
5	**PdNPs/TMC**	**K_2CO_3**	**Water**	**99**
6	PdNPs/TMC	—	Water	Nil
7	PdNPs/TMC	Et_3N	Water	34
8	PdNPs/TMC	NaOAc	Water	49
9	PdNPs/TMC	Na_2CO_3	Water	46
10	PdNPs/TMC	Cs_2CO_3	Water	70
11	PdNPs/TMC	K_3PO_4	Water	66
12	PdNPs/TMC	K_2CO_3	Water	80[g]
13	PdNPs/TMC	K_2CO_3	Hexane	Nil
14	PdNPs/TMC	K_2CO_3	Toluene	10
15	PdNPs/TMC	K_2CO_3	Acetone	35
16	PdNPs/TMC	K_2CO_3	Acetonitrile	40
17	PdNPs/TMC	K_2CO_3	EtOH	53
18	PdNPs/TMC	K_2CO_3	DMSO	65
19	PdNPs/TMC	K_2CO_3	DMF	75

[a] Reaction conditions: iodobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), catalyst; base (2 mmol), 3 mL solvent, 80 °C, 14 h. [b] Isolated yield. [c] 24 h. [d] 0.1 mmol. [e] 10 mg TMC + 0.1 mmol Pd(II). [f] 0.1 mmol EA/Pd(II)acetate. [g] 1 mmol base.

The formation of PdNPs in colloidal solution is controlled by varying the concentration of EA from 0.1 equiv. to 0.5 equiv. for 1 equiv. of Pd(II) acetate and monitored by UV-Vis, absorption and color changes. The optimum concentration was found to be 0.5 equiv. of EA for 1 equiv. $Pd(OAc)_2$, half of the equivalent of EA is found to be enough for the formation of PdNPs in aqueous medium at 50 °C for 6 h. The formation of PdNPs is easily monitored through naked eye and excess addition doesn't make any further change. The orange red color of Pd(II) solution

Table 2 Suzuki reaction of aryl halides with various substituted boronic acids in the presence of TMC supported PdNPs catalyst[a]



S. no.	Aryl boronic acid	X	T h^{-1}	Product	Yield[b]
1	Phenylboronic acid	I	14	3	99
2	Phenylboronic acid	Br	14	3	81
3	Phenylboronic acid	Cl	14	3	61
4	(3,4-Dimethoxyphenyl)boronic acid	I	14	3a	98
5	(3,4-Dimethoxyphenyl)boronic acid	Br	18	3a	81
6	(4-Nitrophenyl)boronic acid	I	14	3b	98
7	(4-Nitrophenyl)boronic acid	Br	16	3b	79
8	[1,1′-Biphenyl]-4-ylboronic acid	I	14	3c	96
9	(3-Methylsulfonyl)phenylboronic acid	I	14	3d	91
10	(3-Methylsulfonyl)phenylboronic acid	Br	14	3d	81
11	(3-Isobutyramido-5-methyl-phenyl)boronic acid	I	14	3e	94
12	(3-Isobutyramido-5-methyl-phenyl)boronic acid	Br	16	3e	78
13	(5-Chloro-2-methylphenyl)-boronic acid	I	14	3f	80
14	Benzo[*d*][1,3]dioxol-5-ylboronic acid	I	14	3g	90
15	(6-Methoxypyridin-3-yl)boronic acid	I	14	3h	87
16	Naphthalen-1-ylboronic acid	I	14	3i	97
17	Naphthalen-1-ylboronic acid	Br	18	3i	82
18	(4-Cyanothiophen-3-yl)boronic acid	I	14	3j	<10
19	Furan-3-ylboronic acid	I	14	3k	84
20	Furan-3-ylboronic acid	Br	18	3k	89
21	Thiophen-2-ylboronic acid	I	14	3l	92
22	(5-Methylthiophen-2-yl)boronic acid	I	14	3m	91
23	(4-Ethoxy-3-fluorophenyl)boronic acid	I	14	3n	99

[a] Reaction conditions: aryl halide (0.5 mmol), aryl boronic acid (0.6 mmol), 20 mg PdNPs/TMC catalyst; K$_2$CO$_3$ (2 mmol), 3 mL water, 80 °C.
[b] Isolated yield.

which appeared at 409 nm band in UV-Vis spectra changed gradually into brown black with incremental addition of EA with concomitant increase in the intensity of absorption (Fig. S1†) indicating formation of PdNPs. After complete addition of EA, a broad band is developed without any peak, which is characteristic of colloidal PdNPs.

Tannins are a family of polyphenolic compounds and their chelating properties towards transition and active redox metals have been reported to form stable complexes with metal ions such as silver, copper, zinc and several other metal ions[51–54] and are shown to play an important role in the formation of metal nanoparticles. Ellagic acid due to its extensive polyphenolic ring system has an affinity towards palladium ions and consequently reduces it to form palladium nanoparticles.

The role of EA in the PdNPs formation in water is also evidenced from FT-IR (Fig. S2a†), with characteristic peaks at 1714 cm^{-1} and 1359 cm^{-1} for C═O and C–O–C groups respectively and a broad peak in the region of 3200–3500 cm^{-1} for phenolic –OH groups of EA. Absence of above peaks in the TMC and PdNPs/TMC solid matrix (Fig. S2b and S2c†) indicates that EA is not present in PdNPs/TMC solid matrix. This also shows that after the reduction, EA is removed from TMC solid matrix during filtration and washing process. Thus in the presence of EA, Pd nanoparticles of different sizes and shapes are formed and this interactions, with EA allows the formation of quinoid structure containing keto–enol system which is similar to that observed in the case of formation of gold nanoparticles in the presence of gallic acid.[49]

The phase and purity of the prepared PdNPs/TMC catalyst are determined from the powder X-ray diffraction (XRD) pattern (Fig. S4†) which shows a broad diffraction with 2θ ranging from 8° to 20°, confirming the presence of solid matrix of the TMC. Besides this, the three diffraction peaks at 2θ values of 39.32°, 45.56°, and 66.82° corresponding to (111), (200) and (220) lattice planes of face centered cubic (fcc) crystalline structure of the PdNPs are also observed. According to the Scherrer equation,[55] the average size of the PdNPs is found to be 4.6 nm, calculated utilizing the 111 lattice plane, which is approximately the same with that observed from TEM images shown in Fig. 1.

Fig. 1a shows the transmission electron microscope (TEM) image of the resultant PdNPs/TMC heterogeneous catalyst. Spherically shaped PdNPs of 3 to 5 nm uniformly dispersed on TMC solid surface are obtained and obviously no aggregation of PdNPs is noticed (Fig. 1a). Fig. 1b and c showed the high resolution TEM (HR-TEM) image and selected area electron diffraction (SAED) of catalyst respectively. This indicates that

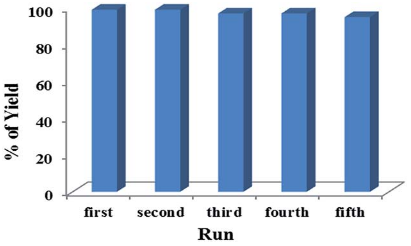


Fig. 2 Reusability of the heterogeneous PdNPs/TMC catalyst in Suzuki reaction.

the PdNPs has a face-centered cubic (FCC) structure which agrees with the recorded powder X-ray diffraction pattern of PdNPs/TMC. Fig. 1d shows average particle size histogram of PdNPs/TMC and it shows that the maximum numbers of PdNPs are present around 3 nm size.

Thus the observed results shows clearly that TMC has the capacity to entrap palladium in good quantity without aggregation of the PdNPs. Along with spherically shaped nanoparticles, cubical PdNPs of 25 nm size are also found to be present (Fig. S5†).

In order to test the catalytic ability of PdNPs/TMC as heterogeneous catalysts, Suzuki reaction between iodobenzene and phenylboronic acid in water using potassium carbonate as a base is chosen as a model reaction. The observed results are given in Table 1. The reaction fails in the absence of catalyst (entry 1) indicating the importance of the catalyst. Poor yield is observed in the absence of support with only Pd(II) (entry 2). With PdNPs/EA also only 49% yield (entry 4) is obtained and an additional handicap is that the catalyst separation from the reaction mixture is difficult. This is due to the fact that PdNPs in solution phase are unstable and showed poor catalytic activity due to a decrease in surface area through aggregation. Surprisingly excellent yield (99%) is observed when the reaction is carried out with PdNPs/TMC as the heterogeneous catalyst.

The nature of base also has a very strong influence on the reaction. No product was obtained in the absence of the base (entry 6). Organic bases show lower activity in coupling reaction (entry 7) while inorganic bases acted efficiently. Inorganic bases other than carbonate bases are less effective and afforded moderate yield of the coupling product. Among the inorganic bases used, K_2CO_3 afforded the excellent result (entries 8–11). However, lowering the mole percentage of base decreases the yield significantly (entry 12).

Table 3 Sheldon test for PdNPs/TMC catalyst[a]

	Yield[b]	
Catalyst	7 h	7 h + 7 h
Pd/TMC	42	43[c]

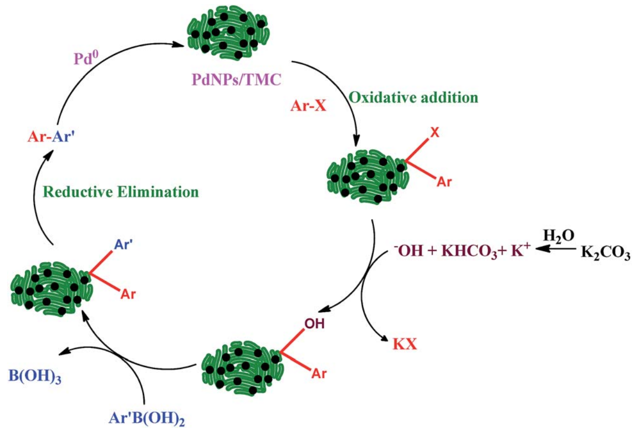
[a] Reaction conditions: phenylboronic acid (1 mmol), iodobenzene (2.0 mmol), catalyst (40 mg), water (3 mL) at 80 °C. [b] Isolated yield. [c] After removing the catalyst.

Generally, Suzuki reaction is performed in organic solvent or in the solvent mixture of water and polar organic solvent such as *N*,*N*-dimethylformamide (DMF) or in water with the addition of surfactant.[56,57] The effect of various solvents is next investigated and results are given in Table 1 (entries 13–19). The reaction fails when hexane is used as a solvent, due to the poor solubility of reactant in hexane (entry 13). The reaction works well when water is used (entries 5 & 13–19) as solvent. This may be due to the fact that water helps in solvation of the organic substrates and the inorganic base. In contrast, poor product formation is observed in less polar solvents such as toluene, acetone & acetonitrile and polar solvents such as ethanol, DMF and DMSO. Thus the optimized reaction conditions for aryl iodide (0.5 mmol) and phenylboronic acid (0.6 mmol) are 20 mg PdNPs/TMC as a catalyst, 2 mmol base, water (3 mL) as a solvent heated at 80 °C for 14 h.

To explore the scope of the reaction further, the present study is extended to various aryl halides and substituted boronic acids carrying either an electron releasing/withdrawing substituents under the optimised reaction conditions. All the reactions proceeded efficiently and resulted in higher yields and the observed results are presented in Table 2. Suzuki reactions of aryl chloride and bromide proceeded with yields of 61% and 81% respectively at 80 °C (entries 2 and 3). In addition, a wide range of functional groups in boronic acids such as alkyl, aryl, nitro, amide and methoxy groups are tolerated. Sterically more hindered boronic acid gave lesser yield (entry 13).

Heterocyclic compounds are difficult substrates to undergo coupling reactions due to their potential coordination with catalysts. Therefore, the scope of this reaction is also extended to various heterocyclic boronic acids such as pyridine, furan and thiophene moiety containing boronic acids (entries 15, 19–22). It is noteworthy to mention that most of the substrates give higher yield. However, very poor yield is observed when heterocyclic rings containing electron withdrawing groups such as cyano group are used (entry 18).

Different substituted boronic acids also gave good yields when coupled with aryl bromide in the Suzuki reaction, though longer reaction time (14 h to 18 h) is needed. However, under



Scheme 2 Plausible mechanism for PdNPs/TMC catalyzed Suzuki reaction in water.

Table 4 Catalytic performance of different supported catalysts in the coupling of phenylboronic acid with iodobenzene (entries 1–9) and bromobenzene (entries 11–15)

S. no.	Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)	Ref.
Coupling between iodobenzene and phenylboronic acid						
1	PdNPs/PS[a]	H_2O–DMF	100	12	100	59
2	PdNPs/chitosan[b]	Xylene	130	4	71	60
3	Pd-S-GaAs[c]	EtOH	80	12	89	61
4	Pd-HP-α-CD[d]	H_2O	60	24	100	62
5	G4-OH PdNPs[e]	EtOH	78	18	98	63
6	G3-OH(Pd)[f]	EtOH	Reflux	24	71	64
7	Pd-G3[g]	40% EtOH	Reflux	24	4	65
8	PdNP[h]	H_2O	80	24	97	66
9	Pd(II) complex[i]	DMF	80	30[j]	50	67
10	PdNPs/TMC	H_2O	80	14	99	This work
Coupling between bromobenzene and phenylboronic acid						
11	Pd-HP-α-CD[d]	H_2O	60	24	71	62
12	G4-OH PdNPs[e]	DMF	153	48	70	63
13	Pd(II) complex[i]	DMF	80	30[j]	23	67
14	Pd-Co/CNPs[k]	EtOH	Reflux	20	77	68
15	Pd-basic zeolites[l]	EtOH–H_2O	50	24	85	69
16	PdNPs/TMC	H_2O	80	14	81	This work

[a] PdNPs dispersed on crosslinked polystyrene polymer. [b] PdNPs stabilized on amino modified chitosan-Schiff base ligand. [c] PdNPs supported on sulphur modified gallium arsenide. [d] Hydroxypropyl-α-cyclodextrin stabilised PdNPs. [e] PdNPs stabilized by poly(amido-amine) dendrimers. [f] PdNPs stabilized by dendrimers. [g] PdNPs stabilized by dendrimer. [h] Homogeneous PdNPs. [i] Bis(oxamato)palladate(II). [j] Reaction time-30 minutes. [k] Pd catalyst supported on Co/CNPs. [l] Pd-containing (0.1% → 4.5%) basic zeolites.

the same reaction conditions catalyst gave poor yield with aryl chloride (entry 3), indicating clearly that, TMC supported palladium catalyst is very effective for the Suzuki coupling of aryl iodide and bromide in water.

The catalyst is also found to be reusable. At the end of the reaction, the collected PdNPs/TMC catalyst is filtered and reused. From the ICP-OES analysis of PdNPs/TMC, the palladium content on the surface of PdNPs/TMC catalyst is found to be 0.00103 mol% for freshly prepared PdNPs/TMC. EDAX analyses carried out for fresh and reused samples show that the palladium content remains same after use (Fig. S6a and S6b†). In order to check the reusability of the catalyst, a series of five consecutive runs are carried out in water at 80 °C with the PdNPs/TMC as heterogeneous catalyst. As shown in Fig. 2, the yield of biaryl decreases only to a smaller extent, even after five cycles, which suggests the good stability of the PdNPs/TMC catalyst.

In order to verify real heterogeneity of PdNPs/TMC catalyst, Sheldon test is performed to evaluate possibility of metal leaching. Thus the reaction mixture after 7 h at 80 °C is filtered and the filtrate is further heated at 80 °C for an additional 7 h. Table 3 clearly show that catalytic activity dropped down when the catalyst was removed from the reaction mixture. The obtained results clearly indicate that there is no appreciable leaching of palladium ions under the present reaction condition (Table 3).

By analogy with previous reports,[58] a plausible three step mechanism as outlined in Scheme 2 is proposed for the PdNPs/TMC catalyzed Suzuki reaction in water. In the first step, the oxidative addition of aryl halides to PdNPs takes place leading to an organopalladium intermediate. In the second step, the organic moiety, Ar′ on boron, is transferred to palladium in a transmetallation process. In this way, the two organic groups are assembled on the same palladium atom *via* palladium–carbon bonds. In the final reductive elimination step, the Ar and Ar′ groups couple with each another to give a new carbon–carbon single bond and Ar–Ar′ is released from palladium and during this process Pd(II) is reduced back to PdNPs.

Table 4 shows the various palladium catalysts which have been tested in the Suzuki–Miyaura cross-coupling of phenylboronic acid with iodobenzene and bromobenzene to produce the corresponding biaryl compounds in various solvents. Compared to these catalyst systems given in Table 4, the TMC supported PdNPs catalyst shows a high catalytic activity (yield = 99% for iodobenzene and 81% for bromobenzene) in the coupling of phenylboronic acid with aryl halides in shorter time in a green solvent, namely water, under the optimized conditions.

Conclusions

In conclusion, we have developed a clean and eco-friendly method to synthesize uniform sized spherical and cubical PdNPs supported on TMC, a modified bio-polymer using EA as a green reducing agent in water. The synthesized palladium nanoparticles are characterized using UV-Vis, FT-IR, powder XRD, HR-TEM image techniques. The synthesis of PdNPs showed excellent catalytic activity in Suzuki reaction of aryl iodide as well as bromide with various phenylboronic acid in the presence of K_2CO_3 as base at 80 °C. Easy separation, the absence of nitrogen atmosphere and good to excellent yield are the other significant outcomes of this protocol. In addition, the reaction works well with various heterocyclic boronic acids and also the catalyst can be easily recovered and reused for at least five runs in the reaction without loss in its activity. This methodology is the first report which has widespread applications for the synthesis of various substituted biaryl compounds using this heterogeneous catalyst under ligand-free conditions. We anticipate that this approach will offer alternative synthetic strategies for the practical construction of substituted biaryl compounds.

Experimental section

PdNPs/TMC (20 mg), aryl halide (0.5 mmol), phenylboronic acid (0.6 mmol), K_2CO_3 (2.0 mmol), water (3 mL) are taken in reaction tube. The tube is heated on a preheated oil bath at a given temperature and magnetically stirred under atmospheric pressure. After the reaction was completed, the mixture was cooled to room temperature. Subsequently, the product and catalyst was filtered from the reaction mixture and washed three times with water (3×10 mL). Then the solid biaryl product was washed with diethyl ether and the organic phase is dried over Na_2SO_4. After evaporation of solvent the compound was analyzed by ^1H & ^{13}C-NMR.

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